



(11) Publication number : **0 518 689 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **92305426.6**

(51) Int. Cl.⁵ : **A01N 25/34, B65D 65/46**

(22) Date of filing : **12.06.92**

(30) Priority : **14.06.91 US 715515**
06.08.91 US 740985
10.12.91 US 805857

(43) Date of publication of application :
16.12.92 Bulletin 92/51

(84) Designated Contracting States :
AT BE CH DE DK ES FR GB GR IT LI LU NL PT
SE

(71) Applicant : **RHONE-POULENC AGROCHIMIE**
14-20, rue Pierre Baizet
F-69009 Lyon (FR)

(72) Inventor : **Chen, Chi-Yu R.**
10004 Whitestone Road
Raleigh, North Carolina, 27615 (US)
Inventor : **Weber, Paul J.**
3515-A Century Oaks Road
Durham, North Carolina, 27713 (US)

(74) Representative : **Bentham, Stephen**
J.A. Kemp & Co. 14 South Square Gray's Inn
London, WC1R 5LX (GB)

(54) **New containerization systems and aqueous formulations.**

(57) A containerisation system comprising a water soluble or water dispersible bag containing a liquid or gel composition comprising a hazardous product, an electrolyte and water and compositions suitable for containing such systems. Typical hazardous products include agrochemicals such as pesticides, plant growth regulators, and plant nutrients. Optionally the composition contains a thickener, a solvent or a dispersant. The water soluble bags used as containerisation systems for these compositions may be made of polyvinylalcohol.

EP 0 518 689 A1

This invention relates to new containerisation systems comprising hazardous products which are nevertheless safe for handling and the environment. It further relates to compositions suitable for containment in such systems.

At present, most hazardous liquids are stored in metal drums or, where smaller quantities are required, in plastic containers.

Hazardous compounds, especially agrochemical compounds, are formulated in various compositions. Liquid compositions are most convenient for farmers because of the relative ease with which they can be handled. There are, nevertheless, difficulties in handling such liquid compositions. There is a danger of spillage or leakage if there are holes in the containers if for example they have been previously used or if they are dropped. Although secure containers resistant to shock can be used, in the event of an accident, for example during transportation, the risk remains of spillage or leakage with rapid loss of liquid, for example leaking onto the ground. There is also a danger of splashing when the farmer is putting the liquid in a tank with water.

It has been difficult to provide a formulation and a container system which safeguards the environment and those handling it, including farmers and transporters.

The present invention seeks to provide a new formulation system to contain agrochemicals which is safe for people and the environment.

The invention further seeks to provide a new formulation system for agrochemicals which is easy to put in a containing system and easy to manipulate by the farmer.

The invention further seeks to provide a new formulations system for agrochemicals which is readily soluble and/or dispersible in water.

The invention further seeks to provide a new formulation system for agrochemicals which is as condensed as possible, using the least amount of space possible.

The invention further seeks to provide a new formulation system to contain hazardous compounds e.g., agrochemicals, which diminishes the risks of pollution.

It is known that liquid agrochemicals may be contained in soluble bags or sachets made from films. Such systems are useful and helpful, but may be improved because the films may crack and break and thus cause spillage of the contained agrochemicals and create contamination problems. In fact, there are a variety of defects which may be present in films, which lead to weaknesses of film and consequently a potential source of leakage. The presence of air bubbles, of dust particles, of foreign materials, of gel particles or thin areas on or in the film are all potential weak points. If a film with such weak points is subjected to much handling or to physical shock, for example

if dropped, the film may fail at any such weak point. This is especially a problem in the agrochemical industry where containers may be subjected to rough or unsafe handling by distributors or farmers.

The invention further seeks to avoid leakage through pinholes in bags containing an agrochemical. Such pinholes are rare, but only one pinhole among thousands of bags is sufficient to be a serious problem, since the liquid going through the pinhole contaminates its environment.

The invention further seeks to avoid breakage of a container which contains an agrochemical formulation. When the container is rigid, there is a certain possibility of simple breakage. With a liquid in a bag this possibility is somewhat reduced, but the liquid still transmits shocks to the bag and there is a problem caused by the hydraulic hammer effect. The invention seeks to avoid, or at least to reduce, this hydraulic hammer effect. It has been proposed to reduce the possibility of breakage by mean of an air space in the bag, but this represents some loss of storage space.

The invention further seeks to provide a composition comprising a hazardous compound which dissipates, as much as possible, the energy of a shock to a container from outside.

The invention further seeks to provide a shock absorbing formulation system for containing agrochemicals, e.g., pesticides (especially insecticides, acaricides and nematocides) herbicides, fungicides, plant protection agents, plant growth regulators or plant nutrients.

It is known to use gel formulations for pharmaceuticals or cosmetics, but the technical problems and the solution for solving such problems are very different from those involved in packaging agrochemicals.

In particular:

there is practically no risk of polluting or contaminating of the environment when handling such products, which is in contrast to pesticides and other agrochemicals;

it is generally sufficient for such gels to have a water insoluble package;

there is practically no exposure to air humidity;

and the size of container used for pharmaceutical or cosmetic purposes is generally very small, compared to that required for agrochemicals.

Thus this does not suggest that water soluble sachets or bags containing gels be used to provide a containerisation system for agrochemicals, which is able to absorb shock efficiently.

Another possibility is to have agrochemicals in the form of wettable powders in a bag which may be water soluble. However, not all agrochemicals may be used in the form of a wettable powder, and even when these powders are wettable, the time to wet the powder (wetting time) may be too lengthy to be practical.

As already discussed, other containing systems for pesticides which are safe for the environment have been proposed in the past, including some containing liquid in soluble bags or sachets. However, up to now the liquids which have been used are hydrophobic and non-aqueous liquids because aqueous liquids can damage the walls of the water soluble bags which contain them, especially for large bags such as one litre bags. Unfortunately, there is a general trend in agriculture to use more and more aqueous formulations because such formulation are safer for the environment and for the people who handle the agrochemicals. Furthermore some agrochemical compounds can in practice be formulated only in an aqueous medium, such as amine salts. In such cases the use of water soluble bags containing a non-aqueous formulation is clearly not practical.

In patent application WO/89/04282 it has been proposed to have aqueous syrup compositions in water soluble bags. That invention is based on the use of an osmosis phenomenon which requires a high concentration of syrup in the composition. The concentration may be increased, of course, by decreasing the amount of water; however, this is detrimental to the dispersibility of an agrochemical composition during tank mixing in the field. Alternatively, the concentration of syrup may be increased by adding sugar, but this is not realistic for agrochemical compositions, for many reasons. In particular, sugar, especially large amounts of sugar, may transform the agrochemical composition to a kind of a bait for warm blooded animals, which is especially undesirable where environmentally safe products are required. Also, the syrup may cause fermentation yielding gas and pressure in the stored product thus shortening the useful life of the agricultural formulation.

The present invention seeks to provide a new aqueous formulations system for hazardous chemicals, especially agrochemicals, which does not damage the water soluble bags containing them and which is based on a completely different principle from the above known packaging technology.

The invention further seeks to provide a new formulation system for agrochemicals which quickly dissolves when put into water and which is not damaged by normal freezing.

The present invention provides a containerisation system comprising a water soluble or water dispersible bag, containing a composition which is a liquid or, more preferably, a gel comprising:

a hazardous product, which is preferably an agrochemical compound;

from 5 to 90%, preferably 8 to 55%, by weight of water; and

an effective amount of electrolyte, preferably salt containing an inorganic cation, more preferably inorganic salt, sufficient to provide or to improve the insolubility in the composition of the film constituting

the wall of the bag which contains the composition, the electrolyte being distributed homogeneously throughout the composition. The electrolyte may be either dispersed or dissolved in the composition.

In one embodiment the composition comprises from 8 to 40% by weight of water.

The invention further provides compositions (or formulations) which are especially suitable for containment in such systems.

Other additives are optional and include:

a surfactant;

a thickener and/or a gelling agent;

an organic solvent (as used herein this word includes a mixture of individual solvents) which is miscible (or at least dispersible and/or emulsifiable) with water, and preferably such that the hazardous product is soluble in the mixture of this solvent and water at the given concentration;

a dispersant;

a secondary thickener; and

other additives, such as stabilizer(s), antifoaming agent(s), buffer(s), antifreezing agent(s).

As a preferred mode of realisation of the invention, the amount of electrolyte in the composition is such that the polymer constituting the wall of the bag is insoluble in a mixture consisting of the same amount of electrolyte as present in said bag and of an amount of water having the same weight or volume as the total composition or formulation of said bag.

More preferably, the polymer constituting the wall of the bag is chosen in such a way that a sample of it remains water soluble in pure water at 20°C after immersion (during at least one day, preferably one week, at 25°C) in a mixture consisting of the same amount of electrolyte as present in said bag and of an amount of water having the same weight or volume as the total composition or formulation of said bag.

In the situation where the hazardous product is a water soluble salt, the compound may be considered both as electrolyte and as hazardous product. However, electrolytes which are not hazardous products may be used together with a hazardous product which is a salt.

Among the gels includes in the compositions of the invention as hereabove defined, some particular gels are preferred, especially those comprising by weight:

5 to 93%, more preferably 25 to 80%, of the active ingredient (hazardous product);

1 to 50%, more preferably 2 to 25%, of the electrolyte; however the precise nature of the limits of amount of electrolyte are determined by the limit of solubility of the water soluble film in the formulation as already defined;

1 to 60%, more preferably 2 to 45%, of surfactant;

0.1 to 50%, more preferably 2 to 10%, of gelling agent (or gellant);

0.1 to 30%, more preferably 1 to 25%, of secondary thickener;

0 to 80%, more preferably 2 to 50%, of solvent;

0 to 20% preferably, 0.1 to 10%, of other additives (as hereinbefore defined); and

a buffer able to adjust the pH of the composition in the range from 3 to 9 in order to improve the solubility of the film of the bag in cold water.

As already discussed, the formulation of the invention may be liquid, but gels are preferred, because they have many favourable properties in relation to the objects of the invention as hereinbefore discussed.

It is known that a gel is generally a colloid in which the dispersed phase has combined with the continuous phase to produce a viscous, jelly-like product (i.e., continuous system); it is also a dispersed system consisting typically of a high molecular weight compound or aggregate of small particles in very close association with a liquid. In the compositions used in the invention, the hazardous product (i.e., active ingredient) may be in a soluble form, or in a dispersed form such as in a suspension.

As used herein, "continuous system" means a material which is visually homogeneous, i.e., one which has the visual appearance of having only one physical phase, but not excluding the possibility of having small solid particles dispersed therein provided these particles are small enough not to constitute a visible separate physical phase.

According to a feature of the present invention, a gel is essentially a material which has a phase difference ϕ between the controlled shear stress and the resulting shear strain such that $\tan \phi$ is less than or equal to 1.5, preferably less than or equal to 1.2. $\tan \phi$ is the tangent of the angle ϕ (or phase difference).

The measurement of ϕ is made by means of a dynamic rheometer. Dynamic rheometers which are appropriate to measure ϕ are known and available commercially. They usually have a flat fixed plate and a rotating cone or plate, or a so-called couette measuring system. Other mechanical systems are also available. Generally the choice of one system or another is made according to the recommendations of the seller of the rheometer, and is adapted to the kind of compound, gel or liquid, which is tested. The particular choice of a specific type of rheometer is something well known by the man skilled in the art of rheology. A rotating plate over another plate or a cone rotating over a plate are often more appropriate when a gel or a viscous liquid is tested. When two kinds of system for the rheometer are possible, similar values of ϕ are actually measured. The cone (or the plate or the couette) is caused to rotate by means of a controlled speed motor; the rotation is a sinusoidal one, i.e., the strain and the angular displacement change as a sine function with time. $\tan \phi$ is equal to the ra-

tio G''/G' , wherein: G' is the storage modulus (represents the behaviour of a perfect solid); G'' is the loss modulus (represents the behaviour of a perfect liquid). G' and G'' are expressed in Pascal for a given rotational speed (radian per second).

G' and G'' , and thus $\tan \phi$, may depend on the amplitude of the oscillations (percentage of strain) of the rheometer; however, there is generally a so-called viscoelastic plateau whereby the values G' and G'' of a gel do not depend substantially on the said amplitude; this means that, in the conditions of the test under the viscoelastic plateau, the structure of the gel is maintained and no destruction of the gel into a liquid happens. Of course, the measurement of G' and G'' of a gel is made under the conditions of this viscoelastic plateau, just because it corresponds to the normal gel structure which is precisely what is tested.

G' and G'' , and thus $\tan \phi$, may also depend on the speed of the oscillations (time to reach the chosen percentage of strain; expressed as radian per second) of the rheometer; however, when the gel is well structured, there is no so much variation from one speed to another. In order to have a reasonable measurement of the properties of a gel, it is generally preferred to operate in conditions whereby the gel is not too much stressed, that is to say at speed such as 1 radian per second. Of course, measurements at higher speed may also be made.

According to another particular feature of the invention, the components of the compositions of the invention are chosen in such a way that they form a material (i.e., gel) having a viscosity of 600 to 30,000 centipoises, more preferably of 1000 to 12,000 centipoises (these viscosities are Brookfield viscosities measured with a viscosimeter in form of a flat plate rotating at 20 revolutions per minute at room temperature, that is to say about 23°C).

According to a particular feature of the invention, when the compositions used in the invention are liquid, their viscosity (as hereinbefore defined) is between 10 and 500 centipoises, preferably of 10 and 300 centipoises.

According to a particular feature of the invention, the components of the composition are chosen in such a way that the gels of the invention have a spontaneity (as hereafter defined) less than 75, preferably less than 25. the spontaneity is assessed according to the following method: A mixture of 1 ml gel with 99 ml water is put into a 150 ml glass tube which is stoppered and inverted through 180° (turned upside down). The number of times required to completely disperse the gel is called the spontaneity.

According to one feature, the gels of the invention preferably have a density greater than 1, preferably greater than 1.05.

The electrolytes which may be used in the invention may, for example (and as a non limiting list of examples), comprise a cation or mixtures of cations

which may include : aluminium, ammonium, antimony, barium, bismuth, cadmium, calcium, cesium, copper, iron, lithium, magnesium, nickel, potassium, rubidium, silver, sodium, strontium, zinc or zirconium ; and of an anion or mixtures of anions or polyatomic anions which may include : acetate, aluminum sulfate, aminechlorides, aminenitrates, aminesulfate, aminethionates, ammonium tartrate, azide, benzene-sulfonate, benzoate, bicarbonate, bisulfite, borate(s), borohydride, borotartrate, borooxalate, bromate, bromide, butyrate, camphorate, carbonate, chlorate, chloride, chlorite, chromate, cinnamate, citrate, cyanate, cyanide, dichromate, disilicate, dithionate, ethyl-sulfate, ferricyanide, ferrocyanate, ferrocyanide, fluoride, fluoantimonate, fluoborate, fluoroacetate, fluorophosphates, fluorosulfonate, fluosilicate, formaldehyde-sulfoxylate, formate, furanacrylate, glycerophosphate, hydrogen carbonate, hydrogen sulfate, hydrogen sulfite, hydrogencyanide, hydrogenophosphate, hydrogensulfate, hydrosulfite, hydroxide, hydroxostannate, hypochlorite, hyponitrite, hypophosphite, iodate, iodide, isobutyrate, lactate, laurate, manganate, meta-aluminate, metaborate, metaperiodate, metasilicate, methionate, methylsulfate, mixed halides, molybdate, nitrate, nitrite, oleate, orthophosphate, orthophosphite, orthosilicate, oxalate, oxalato-ferrate, oxide, oxides, perborate, perchlorate, perchlorate, permanganate, peroxide, peroxydisulfate, phenolsulfonate, phenoxide, phosphate, polybromides, polychlorides, polyfluorides, polyiodides, polysulfides, propionate, pyrosulfate, pyrosulfite, salicylate, sesqui-carbonate, silicate, silicate, sorbate, stannate, stearate, succinate, sulfamate, sulfanilate, sulfate, sulfide, sulfite, tartrate, thiocarbamate, thiocyanate, thiosulfate or valerate; either in their coordinated, anhydrous or hydrated forms.

Preferred electrolytes (when the hazardous product is not a salt) are those wherein the cation is inorganic, and/or those which are an inorganic salt.

As used herein, "surfactant" means an organic material, which is able to substantially reduce the surface tension of water which is 73 dynes/cm at 20°C.

Preferred surfactants are water soluble or water dispersible surfactants, which may be nonionic or anionic or cationic or may have more than one of these characters. The surfactant(s) satisfy the following test; the hazardous product (50 g) and the surface-active adjuvant (5 g) are added to an amount of water, at 50°C, which is sufficient to bring the volume of the mixture to 100 ml; the mixture is agitated so as to give a homogeneous emulsion and this is left to stand for 30 minutes at 50°C in a graduated cylinder, the amount of oily layer which may have separated out (and thus formed a distinct liquid phase) must then be less than 20 ml.

Preferred gels of the invention are also those which contain a surfactant which has a high HLB (hydrophile-lipophile balance) and which is able to form

above 70°C, preferably above 50°C, a liquid phase with the active ingredient (hazardous product).

The surfactants which may be used in the invention may be selected from the following list (which is non limitative; provided that the physical requirements of the surfactant are met) : alkanolamides, polycondensates of ethylene oxide with fatty alcohols, fatty esters, or fatty amines, or substituted phenols (particularly alkylphenols or arylphenols); block copolymers with ethoxy and propoxy groups; esters of fatty acids with polyols such as glycerol or glycol; polysaccharides; organopolysiloxanes; sorbitan derivatives; ethers or esters of sucrose or glucose; salts of lignosulphonic acids, salts of phenyl sulphonic or naphthalene sulphonic acids, diphenyl sulfonates; alkylaryl sulfonates; sulfonated fatty alcohols or amines or amides; poly condensates of ethylene oxide with fatty acids and their sulfate or sulfonates derivatives; salts of sulphosuccinic or sulfosuccinamic acid esters; taurine derivatives (particularly alkyltaurates); betaine derivatives; phosphoric esters of alcohols or of polycondensates of ethylene oxide with phenols; and sulphate, sulphonate and phosphate functional derivatives of the above compounds.

As used herein, "gelling agent" means a material corresponding to the active ingredient in such a way that, when mixed, at 50/50 w/w and 25°C with water, where the active ingredient is either soluble or dispersible, a gel can be obtained. Preferred gelling agents may be either liquid or solid at 23°C and are soluble at less than 10 % in the aqueous mixture of active ingredient and surfactant or simply dispersible in the aqueous mixture.

More specifically organic water soluble gums and resins which may be used in the invention as gelling agents include, but are not limited to the following : alginates, alkyl and hydroxyalkylcellulose, carboxymethylcellulose, carrageenan, guar gum, agar, gum arabic, gum ghatti, gum karaya, gum tragacanth, hydroxyethylcellulose, hydroxypropylcellulose, locust bean gum, pectins, polyacrylamide, polyacrylic acid, polyethylene glycol, poly(ethylene oxide), polyvinyl alcohol, polyvinylpyrrolidone, starch, tamarind gum, and xanthan gum.

The gelling agents can be inorganic as well. Examples include, but are not limited to, the following : natural clays like kaolins, serpentines, smectites (montmorillonites), bentonites, illites, glauconite, chlorites, vermiculites, mixed-layer clays, attapulgite, saponite and sepiolite. Synthetic clays such as synthetic smectic clays, silicates and fluorosilicates may also be used.

As used herein, "hazardous product" means a product which may cause damage to the environment or be injurious to a person handling it. According to one main and preferred feature of the invention, the hazardous product is an active ingredient which is an agrochemical, and more precisely a plant protection

agent or pesticide (particularly herbicide, insecticide, fungicide, acaricide or nematocide) or a plant growth regulator or plant nutrient or an adjuvant for the activity for plants as activity promoters including penetrating agents, synergists, antidotes, sticking agents, spreaders, activators, compatibility agents. The invention is not limited to some specific agrochemicals; a list of many insecticides, nematicides, herbicides, fungicides, acaricides, and plant growth regulants, and their corresponding ammonium and mono-/divalent metal salts, and amine salts or their acid salts which can be used in the invention is given hereafter:

1-Naphthylacetic acid, 2,4,5-T, 2-(2-chlorobenzyl)-4-dimethyl-1,2-oxazolidin-3-one, Acetochlor, Alachlor, Aldrin, Alphacypermethrin, Ametryn, Amitraz, Amitrole, Anilofos, Asulam, Atrazine, Azinphos and its derivatives, Barban, Bentazole, Bentazone, Benzoylprop-Ethyl, Bifenox, Bifenthrin, Binapacryl, Bitertanol, Bromoxynil, Bupirimate, Butachlor, Butralin, Carbaryl, Carbetamide, Carbosulfan, Chlordane, Chlordimeform, Chlorfenvinphos, Chlorfluazuron, Chlorothalonil, Chlorpyralid, Chlorpyrifos, Chlorsulfuron, Cinmethylin, Clomazone, Cyanazine, Cycloxydim, Cycocel, Cyfluthrin, Cyhalothrin, Cypermethrin, Deltamethrin, Demeton, Demeton-S-Methyl, Desmedipham, Diallate, Diazinon, Dichlone, Dichlorophen, Dichlorprop, Dichlorvos, Diclofop-methyl, Dicofof, Dicrotophos, Dieldrin, Diethatyl-Ethyl, Difenconazole, Diflufenican, Dimethachlor, Dimethametrynn, Dimehoate, Dinocap, Dinoseb Acetate, Dinoseb, Dinoterb, Dioxacarb, Disulfoton, Dodemorph Acetate, Ebufos, Edifenphos, Endosulfan, Endrin, EPN, Esfenvalerate, Ethiofencarb, Ethion, Ethirimol, Ethofumesate, Ethoprophos, Ethoxyquin, Etrimfos, Fenethanil, Fenitrothion, Fenobucarb, Fenoxaprop-Ethyl, Fenopropathrin, Fenpropidin, Fenpropimorph, Fensulfothion, Fenthion, Fenvalerate, Flamprop and Its Derivatives, Fluazifop-p-butyl, Fluazifop-butyl, Fluchloralin, Flucytrinate, Flumetralin, Fluometuron, Fluoroglycofen-Ethyl, Fluotrimazole, Flusilazol, Fluvalinate, Formothion, Furathiocarb, Glufosinate-Ammonium, Heptachlor, Hezptenophos, Hydroprene, Imazethapyr, Iodofenphos, Ioxynil, Iprobenfos, Iprodione, Isazophos, Isafenphos, Isoprocarb, Isoproturon, Lambda-Cyhalothrin, Lindane, Linuron, Malathion, Mancozeb, MCPP, Mecoprop, Mephosfolan, Merphos, Metalaxyl, Methacrifos, Methamidophos, Methidathion, Methomyl, Methoprene, Methyl Isothiocyanate, Methylparathion, Metolachlor, Metribuzin, Metsulfuron, Mevinphos, Mexacarbate, Miclobutanil, Molinate, Monalide, Monolinuron, Napropamide, Nitrofen, Omethoate, Oryzalin, Oxadiazon, Oxydemeton-Methyl, Oxyfluorfen, Parathion, Parathion-Methyl, Penconazole, Pendi-methalin, Permethrin, Phenisopham, Phenmedipham, Phorate, Phosalone, Phosfolan, Phosphamidon, Phoxim, Piperophos, Pirimicarb, Pirimiphos-Ethyl, Pirimiphos-Methyl, Pretilachlor, Prochloraz, Pro-fenofos, Profluralin, Promecarb, Prometon, Prome-

tryn, Propachlor, Propanil, Propargite, Propetamphos, Propham, Propiconazole, Propoxur, Propyl 3-Tert-Butylphenoxyacetate, Propyzamide, Prosulfocarb, Protiphos, Pyrazophos, Quinalphos, Quintozene, Quizalofop-Ethyl, Sethoxydim, SN-106 279, Sulprofos, Tebuconazole, Tebutam, Tebuthiuron, Tefluthrin, Temephos, Tetrachlorvinphos, Thiobencarb, Thiodicarb, Tiometon, Tralkoxydim, Tri-Allate, Triadimefon, Triadimenol, Triazophos, Tribufos, Trichloronat, Tridemorph, Trifluralin, and Triforine, Vamidothion,

(2-Naphthylloxy)acetic acid, 2,3,6-TBA, 2,4,5-T, 2,4-D, 2,4-DB, 2,4-DES, 2,4-DP, 2-(1-Naphthyl)acetic acid, 2-Phenylphenol, 4-Indol-3-yl-butyric acid, Acifluorfen, Alloxymid, Ammonium sulphamate, Benzolin, Bordeaux mixture, Bromacil, Bromoxynil, Butylamine, Chloramben, Chlorfenac, Chlormequat, Chloroacetic acid, Chlorphonium, Dalapon, Daminozide, Dicamba, Dichlorophen, Difenzoquat, Dikegulac, Dimethylarsinic acid, Dinoseb, Dinoterb, Diquat, DNOC, Dodine, Endothal, Ethepon, Fenaminosulf, Fenopop, Fluoroacetamide, Formaldehyde, Fosamine, Fosetyl, Gibberellic acid, Glufosinate, Glyphosate, Imazalil, Imazapyr, Imazaquin, Indol-3-ylacetic acid, Ioxynil, Kasugamycin, Maleic anhydride, MCPA, MCPB, Mecoprop, Mepiquat, Mercuric chloride, Mercurous chloride, Metham, Methylarsonic acid, Mevinphos, Monocrotophos, Nabam, Naphtenic acid, Nap-talam, Nicotine, Oxamyl, Paraquat, Pentachlorophenol, Phosfolan, Phosphamidon, Picloram, Piproctan-yl, Polyoxin, Propamocarb, Sodium chlorate, Sodium fluoride, Sodium fluoroacetate, Sodium hexa-fluorsilicate, Strychnine, TEPP, Triclopyr and Validamycin.

Agrochemicals which are in the form of salts or water soluble salts may be, generally, simple amines derivatives or ammonium or monovalent metal or acid halide or sulfate derivatives. The active ingredients which are in a salt form, may be more particularly in the form of a salt of an amine or of ammonium, sodium, potassium, lithium, ammonium, alkanolamines, and simple alkyl or fatty amines. Salts of glyphosate or 2,4-D are preferred, as well as isopropylammonium salt of glyphosate.

The following derivatives of these agrochemicals are found to be feasible (but is not limited to) : benzoate, phenate, mono- and di- carboxylate, alkylamine salt, quaternary ammonium salt, phosphonium salt, hydrogen sulfate salt, pyrazolium salts, arsinates, guanidine, benzenediazosulfonate, acetamide, phosphonate, phosphinate, imidazole, piperidinium, carbamate, arsonate, vinyl phosphate, dithiocarbamate, naphthylacetate, bypyridinium, pyrophosphate, pyridyloxyacetate, phosphorothioate.

In order to assess whether a surface-active adjuvant possesses dispersing properties and may be a dispersant according to the invention, the following test is carried out: an aqueous suspension (100 ml)

containing kaolin or atrazine (50 g), in the form of solid particles having a particle size between 1 and 10 microns, and surfactant (surface-active adjuvant) (5 g) is left to stand at 20°C for 30 minutes in a graduated cylinder. After standing, nine-tenths (9/10) of the volume of the suspension, situated in the upper part of the suspension, is removed, without agitation, and the solids content (residue after evaporation of the water) of the remaining one-tenth (1/10) is measured. This solids content must not exceed 12 % by weight of the solids content of 100 ml of the suspension on which the test is carried out. Kaolin is used when the dispersing agent is able to disperse a hydrophilic solid. Atrazine is used when the dispersing agent is able to disperse a hydrophobic solid.

The dispersant which may be used in the invention includes, but is not limited to, the following : salts of lignosulfonic acids such as calcium lignosulfonate, salts of phenyl sulfonic or naphthalene sulfonic acids, condensed naphthalene sulfonic acid; poly condensates of ethylene oxide with fatty alcohols or fatty acids or fatty esters or fatty amines, or substituted phenols (particularly alkylphenols or arylphenols); salts of sulfosuccinic acid esters, such as sodium sulfosuccinate; taurine derivatives (particularly alkyltaurates); phosphoric esters of alcohols or of polycondensates of ethylene oxide with phenols; esters of polyols and of fatty acids or sulfuric acid or sulfonic acids or phosphoric acids; glyceryl esters, especially esters with fatty acids such as glyceryl stearate; ethylene glycols and the like.

The secondary thickener is a compound which increases the viscosity of a gel or a liquid. The secondary thickener which may be used includes, but is not limited to, the following: alkyl and hydroxyalkylcellulose, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, locust bean gum, polyacrylamide, polyacrylic acid, polyethylene glycol, poly(ethylene oxide), polyvinyl alcohol, polyvinylpyrrolidone, vinylpyrrolidone-maleic anhydride copolymers, vinylpyrrolidone-vinyl acetate copolymers, methyl vinyl ether-maleic anhydride copolymers, alkylated vinylpyrrolidone polymers, starch, xanthan gum, glycols, silica, titanium dioxide and zeolites. They may have a synergistic effect with the gellant in raising viscosities of the liquid mixture or gel.

The gels of the invention can be prepared or manufactured by any known method. A convenient way is to mix together the different constituents of the mixture/composition and to stir them, optionally with grinding or milling and/or heating. The constituents of the composition may be added and mixed randomly or added in several various manners which more conveniently achieve the desired gel properties. As is known to one of ordinary skill in the art, such addition may depend upon the physical and chemical nature of the individual constituents, their combination(s), and the desired final gel. In this regard, sometimes it

is easier to operate with a slow addition of the constituents of the composition.

The present invention includes also containerization systems which comprise water soluble or water dispersible bags containing the formulations or compositions as hereabove defined, especially the gel(s).

The chemical nature of the enveloping film constituting the bags which may contain the composition/gels of the invention can vary quite widely. Suitable material are water soluble (or possibly water dispersible) materials which are insoluble in the organic solvents used to dissolve or disperse the agrochemical active ingredient. Specific suitable materials include polyethylene oxide, such as polyethylene glycol; starch and modified starch; alkyl and hydroxyalkylcellulose, such as hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropyl cellulose; carboxymethylcellulose; polyvinylethers such as poly methyl vinyl ether, poly(2,-4-dimethyl-6-triazolyethylene); poly (vinylsulfonic acid); polyanhydrides; low molecular weight melamine-formaldehyde resins; low molecular weight urea-formaldehyde resins; poly(2-hydroxyethyl methacrylate); polyacrylic acid and its homologs; but preferably the enveloping film comprises or is made from polyvinylalcohol (PVA). Mixtures of polymers or multilayered films may also be used.

As hereabove discussed, the choice of a specific material for the film of the water-soluble bag may be coordinated with the choice of the electrolyte. More preferably, the polymer of the film is chosen in such a way that a sample of the film, after immersion in an aqueous solution of the electrolyte during one day (the conditions of this immersion are such that the film is not dissolved at all during this test), remains water soluble in pure water at 20°C.

Preferred material for constituting the bags for the gels of the invention are polyethylene oxide or methylcellulose, or polyvinylalcohol. When polyvinylalcohol is used, it is advantageously a 40-100 %, preferably 80-99 % alcoholysed or hydrolysed, polyvinyl acetate film.

The water soluble films which are used to make the water soluble bags are known. In order to make a bag, the film needs to be shaped (possibly partially sealed) and then filled with the gel. Generally the gels are able to flow, even if it is a slow rate due to the high viscosity. The container which is used to contain the gels was not used up to now in the agriculture field.

The size of the bag is such that the final (full) bag has a volume generally comprised between 50 ml and 3000 ml, particularly between 150 ml and 1000 ml. The particular size may depend on the normal rate of the active ingredient.

The thickness of the wall of the bags in the invention is generally between 5 and 500 microns, preferably 10 and 150 microns.

According to another feature, the bag of the invention is filled to at least 60% of capacity with the

agrochemical composition-containing substance, more preferably to at least 70% of capacity, still more preferably 80 to 99% of capacity and most preferably 85 to 95% of capacity. The bag is preferably not filled to complete capacity because the unused capacity gives the bag shock resistance, i.e., resistance to breakage when dropped, transported or stored. This unused capacity may or may not contain air or an inert gas. An absence of air or inert gas in the unused capacity further improves shock resistance. However, in deciding how much unused capacity, or absence of air or inert gas, to provide, the advantages of shock resistance must be balanced against the need, if any, for shock resistance and the cost of providing shock resistance. For example, if the bag is stored and/or transported in a shock absorbing container, then it may not be as helpful to provide this unused capacity.

Also, the capacity to which the bag is filled, and whether the unused capacity does or does not contain air or inert gas, is affected by whether it is desired to have the bag sink or float. Whether the bag sinks or floats will depend not only on the unused capacity, but also on the density of the bag contents.

When filled with the formulation hereinbefore described, the bag has to be finally sealed, generally heat sealed, to be closed and/or hermetically sealed.

The following examples are given for illustrative purposes and should not be understood as restricting the invention.

In, these examples, the surfactant satisfies to the test requirement hereabove defined, and, where a gel is described, η (phi) is less than 1.5 .

EXAMPLE 1

A liquid composition is made by stirring at 25°C a mixture of:

active ingredient: (2,4-dichlorophenoxy) acetic acid dimethylamine : 50 %

Electrolyte : sodium sulfate, anhydrous 5 %

Water : 45 %

The mixture was stirred until each component was dissolved or dispersed.

The Brookfield viscosity of the mixture is 200 centipoises.

The emulsion stability was good in the hereabove described test.

900 g of this liquid are put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the liquid and of the bag containing the liquid was 1.1. This bag was then stored at room temperature for 2 months. No breaking or leakage was observed.

A bag identical in composition, capacity and contents to the hereabove-described bag containing 1,000 g of the liquid was prepared. This bag was put

into a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 2 minutes. There was no clogging in the filter which was a 100 mesh screen.

EXAMPLE 2

The procedure of example 1 was repeated, except that the following adjuvant was used to get an aqueous gel :

Gelling agent : montmorillonite 2 %

The amount of water is reduced to 43 %

The Brookfield viscosity of the gel was 2000 centipoises

The emulsion stability was good in the above described test.

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble, thickness : 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.15 .

The bag was then dropped 10 times from 1.2 m. above the ground. No breaking or leakage was observed.

The bag was put into a tank containing water under gently agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 3 minute interval. There was no clogging in the filter which was a 1000 mesh screen.

EXAMPLE 3

The procedure of example 2 was repeated, except the following active ingredient was used:

Active ingredient : 4-(2,4-dichlorophenoxy)butyrate, diethanolamine 57.0 %

The amount of water is reduced to 36 %

The Brookfield viscosity of the gel was 3000 centipoises

The emulsion stability was good in the above described test.

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness : 55 microns). The bag, which was almost full (95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.14.

The bag was then dropped 10 times from 1.2 meter above the ground. No breaking or leakage was observed.

The bag was put into a tank containing water under gently agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 3 minutes interval. There was no clogging in the filter which was a 100 mesh screen.

EXAMPLE 4

The procedure of example 1 was repeated, except the following adjuvant was used to get an aqueous gel :

Gelling agent : xanthan gum 2 %

The amount of water is reduced to 43 %

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.15.

The bag was then dropped 10 times from 1.2 meter the ground. No breaking or leakage was observed.

The bag was put in a tank containing water under gently agitation. (that is to say such as that obtained with pump recycling). It was dispersed within a 2 minutes interval. There was no clogging in the filter with was a 100 mesh screen.

EXAMPLE 5

An aqueous gel composition was made by wet milling at 25°C a mixture of:

Active ingredient : atrazine 40 %

Electrolyte : sodium tripolyphosphate, anhydrous 5 %

Anionic Emulsifier : phosphate ester 2 %

Nonionic emulsifier, nononylphenol ethoxylate : 2 %

Gelling agent : montmorillonite : 1 %

Water : 50 %

The mixture was ground to 5 microns particle size and homogeneous.

The Brookfield viscosity of the gel was 1500 centipoises.

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.2.

The bag was stored at room temperature for 6 months. No breaking or leakage was observed.

A bag identical in composition, capacity and contents to the hereabove-described bag was prepared. This bag was put into a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 10 minutes interval. There was no clogging in the filter with was a 100 mesh screen.

EXAMPLE 6

The procedure of example 5 was repeated, except the following active ingredient and adjuvants were used:

active ingredient: carbaryl 46 %

Electrolyte : ammonium sulfate 6 %

Gelling agent : colloidal magnesium aluminum silicate 0.4 %

Dispersant : sodium alkyl naphthalene sulfonate 1.5 %

Thickener: xanthan gum 0.05 %

The Brookfield viscosity of the gel was 2000 centipoises.

The emulsion stability was good in the above described test.

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.13.

The bag was then dropped 10 times from 1.2 meter above the ground. No breaking or leakage was observed.

The bag was put in a tank containing water under gently agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 3 minutes interval. There was no clogging in the filter with was a 100 mesh screen.

EXAMPLE 7

The procedure of example 5 was repeated, except that the following active ingredient and adjuvants were used :

active ingredient: 2,4-dichlorophenoxyacetic acid, 40.0 %

Electrolyte : potassium chloride 9.0 %

Gelling agent : colloidal smectite 1.0 %

Anionic emulsifier : phosphate 2.0 %

The Brookfield viscosity of the gel was 1500 centipoises.

The emulsion stability was good in the above described test.

1000 g of this gel was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the gel and of the bag containing the gel was 1.10.

The bag was then dropped 10 times from 1.2 meter above the ground. No breaking or leakage was observed.

The bag was put into a tank containing water under gently agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 3 minutes interval. There was no clogging in the filter which was a 100 mesh screen.

EXAMPLE 8

An oil in water emulsion liquid composition was

made by homogenization at 25°C a mixture of :

Active ingredient : 2,4 D isooctyl ester: 50.0 %

Electrolyte : ammonium sulfate 5.0 %

Thickener : titanium dioxide 2.0 %

Nonionic emulsifier : nonylphenol ethoxylate 3.0 %

Water : 40 %

The Brookfield viscosity of the homogeneous mixture was 500 centipoises.

1000 g of this liquid was put into a 1 liter bag made of a film of PVA (88 % hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which was almost full (about 95 % v/v), was heat sealed. The density both of the liquid and of the bag containing the liquid was 1.1.

The bag was then stored at room temperature for 2 months. No breaking or leakage was observed.

A bag identical in composition, capacity and contents to the hereabove-described bag was prepared. This bag was put into a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It was dispersed within a 2 minutes interval. There was no clogging in the filter which was a 100 mesh screen.

Claims

1. A containerisation system comprising a water soluble or water dispersible bag containing a composition which is a liquid or a gel comprising: a hazardous product; from 5 to 90% by weight of water; and an effective amount of electrolyte sufficient to provide or to improve the insolubility in the composition of the film constituting the wall of the bag, the electrolyte being distributed homogeneously throughout the composition.
2. A containerisation system according to claim 1 wherein the hazardous product is an agrochemical.
3. A containerisation system according to claim 1 or 2 wherein the hazardous product is a pesticide, a herbicide, an insecticide, a fungicide, an acaricide or a nematocide.
4. A containerisation system according to any one of the preceding claims wherein the composition comprises from 8 to 55% by weight, water.
5. A containerisation system according to any one of the preceding claims wherein the hazardous product is distinct from the electrolyte.
6. A containerisation according any one of claims 1 to 4 wherein the hazardous product and the elec-

trolyte are the same.

7. A containerisation system according to any one of the preceding claims wherein the composition further comprises one or more of the following: at least one surfactant, a thickener and/or a gelling agent, an organic solvent, a dispersant, a secondary thickener, a stabilizer, an antifoaming agent, a buffer or an antifreezing agent.
8. A containerisation system according to any one of the preceding wherein the hazardous product and the film of the wall of the water soluble bag are such that a sample of the film, after immersion in an aqueous solution of the electrolyte during one day at 25°C, remains water soluble in pure water at 20°C.
9. A containerisation system according to any one of the preceding wherein the electrolyte is a salt.
10. A containerisation system according to claim 9, wherein the salt has an inorganic cation.
11. A containerisation system according to claim 10, wherein the salt is inorganic.
12. A containerisation system according to any one of the preceding claims wherein the composition comprises by weight: 5 to 93% of hazardous product; 1 to 50% of electrolyte; 1 to 60% of surfactant; 5 to 90% of water; 0.1 to 50% of gelling agent; 0.1 to 30% of secondary thickener; 0 to 80% of solvent which is miscible with or dispersible in water; 0 to 25% of dispersant; 0 to 20% of other additives; and optionally, a buffer able to adjust the pH of the composition with the range from 3 to 9.
13. A containerisation system according to claim 12 wherein the composition comprises by weight: 25 to 80% of hazardous product; 2 to 25% of electrolyte; 2 to 45% of surfactant; 8 to 55% of water; 2 to 10% of gelling agent; 1 to 25% of secondary thickener; 2 to 50% of solvent; 2 to 8% of dispersant; and 0.1 to 10% of other additives.
14. A containerisation system according to any one of the preceding claims wherein the composition is a liquid.

15. A containerisation system according to any one of claims 1 to 13 wherein the composition is a gel.
16. A containerisation system according to any one of the preceding claims wherein the hazardous product is dissolved in the composition. 5
17. A containerisation system according to any one of claims 1 to 15 wherein the hazardous product is dispersed in the composition. 10
18. A containerisation system according to claim 14, 15 or 16, wherein the composition is a gel having a phase difference ϕ between the controlled shear stress and the resulting shear strain such that $\tan(\phi)$ is less than or equal to 1.5. 15
19. A containerisation system according to any one of claims 14 to 18 wherein the composition is a gel having a Brookfield viscosity of 600 to 30,000 centipoise. 20
20. A containerisation system according to any of claims 14 to 19, wherein the composition is a gel having spontaneity less than 75. 25
21. A containerisation system according to any one of the preceding claims, wherein the electrolyte comprises:
 a cation or mixtures of cations selected from:
 aluminium, ammonium, antimony, barium, bismuth, cadmium, calcium, cesium, copper, iron, lithium, magnesium, nickel, potassium, rubidium, silver, sodium, strontium, zinc and zirconium; and
 an anion or mixture of anions selected from:
 acetate, aluminium sulfate, aminechloride, aminenitrate, aminesulfate, aminethionate, aminethionates, ammonium tartrate, azide, benzene-sulfonate, benzoate, bicarbonate, bisulfite, borate, borohydride, borotartrate, borooxalate, bromate, bromide, butyrate, camphorate, carbonate, chlorate, chloride, chlorite, chromate, cinnamate, citrate, cyanate, cyanide, dichromate, disilicate, dithionate, ethylsulfate, ferricyanide, ferrocyanate, ferrocyanide fluoride, fluoantimonate, fluoborate, fluoroacetate, fluorophosphate, fluorosulfonate, fluosilicate, formaldehyde-sulfoxylate, formate, furanacrylate, glycerophosphate, hydrogen carbonate, hydrogen sulfate, hydrogen sulfite, hydrogencyanide, hydrogenophosphate, hydrogensulfate, hydrosulfite, hydroxide, hydroxostannate, hypochlorite, hyponitrite, hypophosphite, iodate, iodide, isobutyrate, lactate, laurate, manganate, meta-aluminate, metaborate, metaperiodate, metasilicate, methionate, methylsulfate, mixed halides, molybdate, nitrate, nitrite, oleate, orthophosphate, orthophosphite, orthosilicate, oxalate, oxalatoferate, oxide, perborate, perchlorate, perchlorate, permanganate, peroxide, peroxydisulfate, phenolsulfonate, phenoxide, phosphate, polybromide, polychloride, polyfluoride, polyiodide, propionate, pyrosulfate, pyrosulfite, salicylate, sesqui-carbonate, silicate, sorbate, stannate, stearate, succinate, sulfamate, sulfanilate, sulfate, sulfide, sulfite, tartrate, thiocarbamate, thiocyanate, thiosulfate or valerate.
22. A containerisation system according to any one of the preceding claims wherein the surfactant is able to form above 70°C a liquid phase with the hazardous product.
23. A containerisation system according to any one of the preceding claims wherein the wall of the bag comprises polyethylene oxide, methylcellulose or polyvinyl alcohol.
24. A containerisation system according to claim 23, wherein the wall of the bag comprises 40 to 100% hydrolysed or alcoholysed polyvinylacetate.
25. A containerisation system according to any one of the preceding claims wherein the bag has a volume, when filled, from 50 and 3,000 ml.
26. A containerisation system according to any one of the preceding claims wherein the bag is filled with the composition to at least 60% of capacity.
27. A containerisation system according to claim 26, wherein the bag is filled with the composition to 85 to 95% of capacity.
28. A composition suitable for containment in a containerisation system as claimed in any one of the preceding claims. 40

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92305426.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P, A	WO - A - 92/01 375 (RHONE-POULENC AGROCHIMIE) * Abstract; claims *	1-8, 15-17, 23, 24	A 01 N 25/34 B 65 D 65/46
P, A	WO - A - 92/01 376 (RHONE-POULENC AGROCHIMIE) * Abstract; claims *	1-8, 15-17, 23, 24	
P, A	WO - A - 92/01 377 (RHONE-POULENC AGROCHIMIE) * Abstract; claims *	1-8, 15-17, 23, 24	
P, A	WO - A - 92/01 378 (RHONE-POULENC AGROCHIMIE) * Abstract; claims *	1-8, 15-17, 23, 24	
P, A	EP - A - 0 457 600 (W.R. GRACE & CO.-CONN.) * Abstract; column 1, lines 1-28; claims *	1-3, 23, 24	
P, A	EP - A - 0 449 773 (CIBA-GEIGY AG) * Abstract; claims *	1-3, 23, 24	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	EP - A - 0 347 220 (MAY & BAKER LIMITED) * Abstract; claims 1-5, 20-28 *	1-3, 23, 24	A 01 N B 65 D C 08 L B 32 B
A	US - A - 4 206 101 (WYSONG) * Abstract; column 1, lines 14-40 *	1-3, 23, 24	
P, A	DE - A - 4 113 786 (RHONE-POULENC AGRICULTURE LIMITED) * Abstract; claims 1-27 *	1-3, 23, 24	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 23-09-1992	Examiner SCHNASS
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.92 (P0401)